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Study on the Preparation of Silica Using Residues of Oil Shale

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Abstract

Usage of oil shale produces abundant oil shale residue, which may not only directly cause serious pollution to the environment, but also result in a waste of resource. In this paper, acid leaching method and alkali soluble method were compared to obtain the optimum processing conditions for the preparation of white carbon black, which was determined as follows: the mass fraction of NaOH was 8 %, the alkali dissolving time was 5 h, and the reaction temperature was 100 °C. Then the performance characteristics of the obtained white carbon black were analysed by XRD, SEM and IR spectroscopy. The results showed that the product of silica has a particle size between 20 – 30 nm and a purity of 98.4 %. Preparation of the high quality white carbon black might be a good way to make sufficient and reasonable use of oil shale residues, which will bring many environmental and social benefits.

Keywords

Residue of oil shale, silica, alkali dissolving, characterization

1. Introduction

With the increasing demands for energy and reduction of available petroleum resources, the long-term oil prices tend to increase. Oil shale has drawn much attention in recent years as an important alternative energy resource. However, the waste residue from each oil shale extraction method is fairly high. Even concerning the maximum oil content of oil shale (around 30 %), there will be 70 % waste residue of the spent oil shale after retorting.[1] The main components of oil shale waste are SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO and SO_3 *etc*. Besides, there are many kinds of trace elements, including poisonous and harmful elements.[2] China and the United States have the largest oil shale ash heap in the world, but now there are only Estonia, Russia, Germany and another six countries utilizing the ash and slag. The analysis of the ash shows that it contains heavy metal elements and trace amounts of radioactive elements, which are very likely to cause pollution in water, soil and surrounding flora and fauna. How to effectively improve the comprehensive utilization of oil shale ash and increase the added value of oil shale resources is a technical problem to be solved.

White carbon black is a porous, white, amorphous substance with a large internal surface area, which has good resistance to acids, and is insoluble in water and acids (except for hydrofluoric acid). It is a kind of promising fine chemical widely used in rubbers, plastics, agrochemicals, paintings, medicines, and so on.[4–6]

Reports on the use of oil shale residue to make silica are prevalent in recent years. However, the experimental results turn out to be not good, and especially the low purity of the product seriously affects its application performance.[7–9] Therefore, in order to improve the application performance of silica generated from oil shale residue, further improvement of the preparation method is necessary.

2. Materials and methods

2.1. Oil shale samples

The oil shale used in this study was obtained from the open pit mine located in Fu Shun (FS), China. It was received as hard, dark grey blocks with no particular smell. After burning, breaking, and lapping, the samples were prepared. The chemical composition of the oil shale residue was obtained by X-ray fluorescence spectrometer (Table 1), in which SiO_2 accounted for more than 60 % of the oil shale residue.

Table 1 – Chemical composition of the semicoke of oil shale analysed by XRF

Tablica 1 – Kemijski sastav polukoksa naftnog škriljevca analiziran XRF-om

Component Sastojak	w / %
SiO_2	63.52
Al_2O_3	26.21
Fe_2O_3	3.13
TiO_2	0.78
CaO	4.31
MgO	0.22
K_2O	1.08
Na_2O	0.76

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2.2. Comparison of alkaline and acid methods

2.2.1. The preparation of silica by acid method

In the acid dissociation method, metal oxides and H_2SO_4 reacted easily to produce soluble metal ions, so that Al_2O_3, Fe_2O_3 could be separated from SiO_2 after filtration. In addition, SiO_2 changed from crystal structure to amorphous structure and silica was obtained.

The reaction equations are:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$

Sulfuric acid of a certain concentration was added into a round-bottom flask, preheated to 90 °C in a constant temperature water bath, with the quick addition of 10 g of the calcined oil shale residue and magnetically stirred.[10–16]

In order to study the influence of the concentration of H_2SO_4 on the leaching rate of SiO_2, adopted were four different concentrations of H_2SO_4 analysis. The outcomes of different concentrations of H_2SO_4 are shown in Table 2.

Table 2 – Leaching rates of SiO_2 at different concentrations of H_2SO_4
Tablica 2 – Brzine izluživanja SiO_2 pri različitim koncentracijama H_2SO_4

$c(H_2SO_4)$ / mol l^{-1}	Leaching rate of SiO_2 / % Brzina izluživanja SiO_2 / %
1.0	18.3
5.0	28.5
8.5	42.3
10.0	44.2

The results showed that the leaching rate of SiO_2 increased along with the concentration of H_2SO_4. When the concentration of H_2SO_4 was low, not only was the leaching rate of silica low, but also the silica colour was not white, suggesting the quality of the product was low. When 1.0 ml H_2SO_4 was used, the colour of the obtained silica was earthy red, indicating Fe^{3+} existed in the white carbon black. The acid dissociation method can exclude Fe^{3+} from the oil shale, thus it can influence the quality of obtained silica effectively.

2.2.2. Preparation of silica by alkaline method

Alkali method mainly uses the reaction of oil shale ash, SiO_2, Al_2O_3 and NaOH to generate water soluble Na_2SiO_3, and separate the Na_2SiO_3 from the other components of the oil shale ash by filtration. To carry out the reaction successfully, the solution pH has to be controlled in a certain range. The reaction equations are:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl$$

In the reaction, 10 g oil shale ash, 30 ml water, and 15 g NaOH was added into a 250 ml three-neck flask, and heated at 95 °C in a water bath to react for about 2 h. The pH was adjusted to 8 – 9 to produce white floc, then filtered. The rest of the residue was the white carbon black.[17–23]

In order to study the influence of the concentration of NaOH on the leaching rate of SiO_2, reactions were carried out in different concentrations of NaOH, and the leaching rates of SiO_2 are shown in Table 3.

Table 3 – Leaching rates of SiO_2 at different concentrations of NaOH
Tablica 3 – Brzine izluživanja SiO_2 pri različitim koncentracijama NaOH

c(NaOH) / mol l^{-1}	Leaching rate of SiO_2 / % Brzina izluživanja SiO_2 / %
0.8	10.2
1.8	35.4
2.8	40.3
3.8	52.8
5.0	58.2

Results showed that the alkali concentration had a significant effect on the leaching rate of SiO_2 (Table 3). By comparing the results listed in Table 2 and Table 3, it can be seen that the prepared silica by alkaline method was much higher than that with the acid extraction method. The alkaline dissolution method is more suitable for the industrial production of silica, so this study adopted the alkali dissolving methods to analyse the influence factors of the silicon extraction rate.

2.3. Influence factors of the alkali dissolving method

2.3.1. Influence of the dissociation temperature

To investigate the influence of dissociation temperature on the leaching rate of SiO_2, the reaction temperature was changed to perform the preparation. The results indicated that by increasing the reaction temperature, the extraction rate of SiO_2 had also increased (Fig. 1), which might be attributed to the improved diffusion and chemical reaction rates at higher temperature.

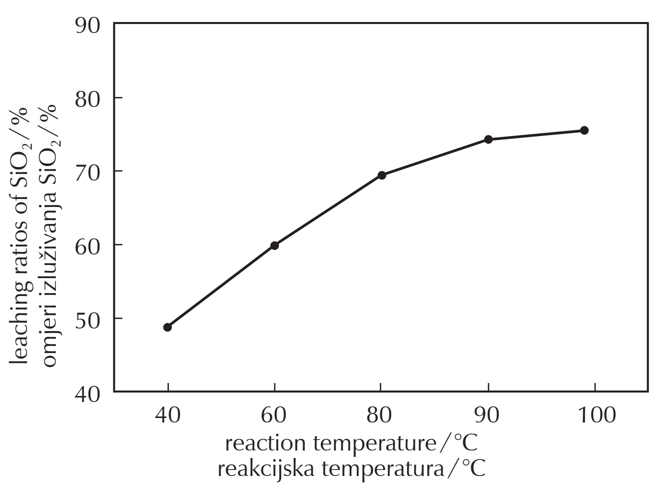

Fig. 1 – Influence of alkali solution temperature on the SiO_2 extraction rate
Slika 1 – Utjecaj temperature lužnate otopine na brzinu ekstrakcije SiO_2

The extraction rate of SiO_2 increased rapidly with temperature up to 90 °C, while it became stable in the range of 90–100 °C. Considering the industrial steam heating, 100 °C might be the optimum extraction temperature.

2.3.2 Influence of the dissociation time

The effect of dissociation time was investigated at various times. As the reaction time proceeded, the extraction rate of SiO_2 increased in the first 5 h, after which it declined. A plausible explanation for this may be due to the separation of Si from the lattice, as the reaction lasted over 5 h, and silicic acid precipitated on the remaining mineral surface, thus slowing down the reaction. Therefore, the appropriate dissociation time for the alkali might be 5 h.

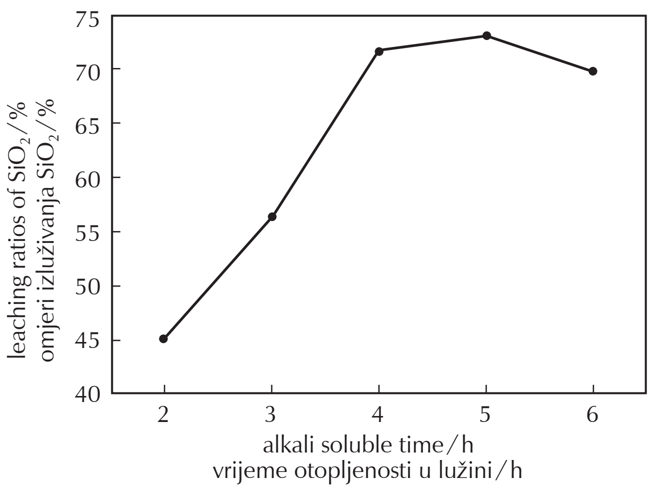

Fig. 2 – Influence of dissociation time on the SiO_2 extraction rate
Slika 2 – Utjecaj vremena disocijacije na brzinu ekstrakcije SiO_2

2.3.3. Determination of the amount of NaOH

The effect of the concentration of NaOH on the extraction rate was investigated.

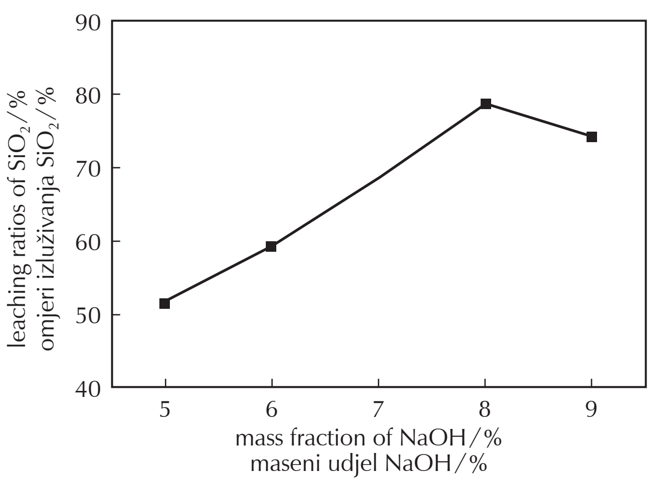

Fig. 3 – Effect of the mass fraction of NaOH on the SiO_2 extraction rate
Slika 3 – Učinak masenog udjela NaOH na brzinu ekstrakcije SiO_2

The results showed that the leaching rate increased as the mass fraction of NaOH increasing up to 8 %. When the mass fraction of NaOH was over 8 %, the extraction rate noticeably declined (Fig. 3). Extracting silica with sodium hydroxide is a solid-liquid multiphase chemical reaction, which may be controlled by diffusion or chemical reaction. In either case, the leaching rate is proportional to the concentration of sodium hydroxide. Because a portion of silica may be attached on the surface of the aluminum dross, the concentration of NaOH should be low; otherwise, the solution will exhibit high viscosity, resulting in difficulties in solid-liquid separation, and thus influencing the extraction rate.

3. Results and discussion

Silica as an important inorganic chemical raw material in industry that has many product indicators, including the contents of impurities, silicon dioxide, and so on. The performance characteristics of the obtained silica in this research was analysed by XRD spectrum, IR spectrum and SEM.[24–25]

3.1. Purity analysis

The purity of the product was analysed by X-ray fluorescence spectrometry, as shown in the following Table 4.

Table 4 – Composition of the silica obtained by the alkali dissolving method
Tablica 4 – Sastav silicijeva dioksida pripravljenog metodom otapanja lužinom

Component Sastojak	w/%
SiO_2	98.4
Al_2O_3	0.124
Fe_2O_3	0.456
TiO_2	0.099
CaO	0.134
MgO	0.086
Cl	0.111
ZnO	0.014
SO_3	0.144
Na_2O	0.428

Results showed that there were very low amounts of impurities in the product.

3.2. XRD analysis

The crystal structure of the product recognition with XRD is shown in Fig. 4.

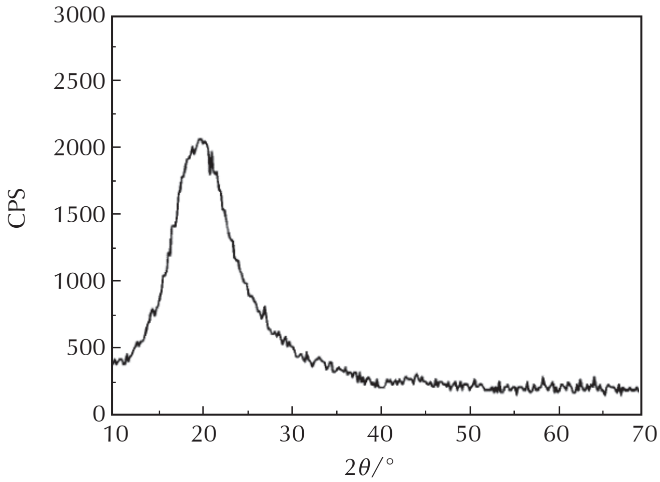

Fig. 4 – XRD spectrum of the silica product
Slika 4 – XRD-spektar proizvoda silicijeva dioksida

The XRD spectrum of the SiO_2 product did not show a sharp crystal diffraction peak, while only amorphous diffraction peaks appeared at 20 – 30°, indicating that the obtained products contained no other crystalline phases, and the product structure was amorphous.

3.3. IR analysis

In the infrared spectrum, the 1100 cm^{-1} and 466 cm^{-1} peaks represented the Si–O–Si bond of antisymetric stretching vibration, while the peak at 950 cm^{-1} represented the bending vibration. The 1640 cm^{-1} absorption peak indicated the bending vibration of surface water H–O–H. The peak at 3400 cm^{-1} indicated the product internal structure of water (Fig. 5).

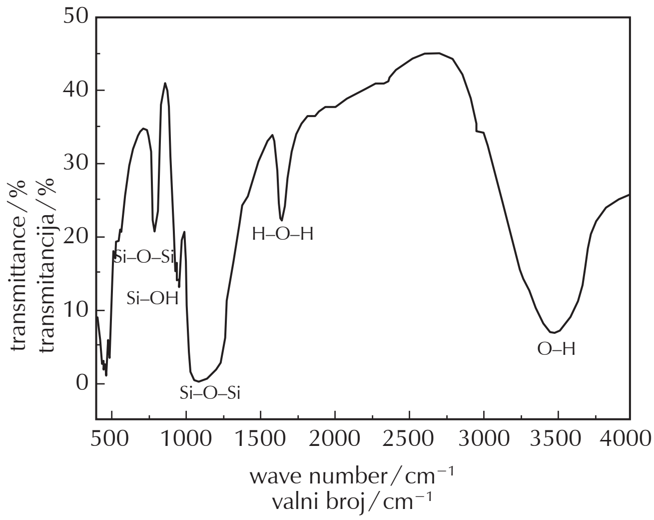

Fig. 5 – Infrared spectrum of the silica product
Slika 5 – Infracrveni spektar proizvoda silicijeva dioksida

3.4. SEM analysis

The results of the scanning electron microscope analysis of the product is shown in Fig. 6.

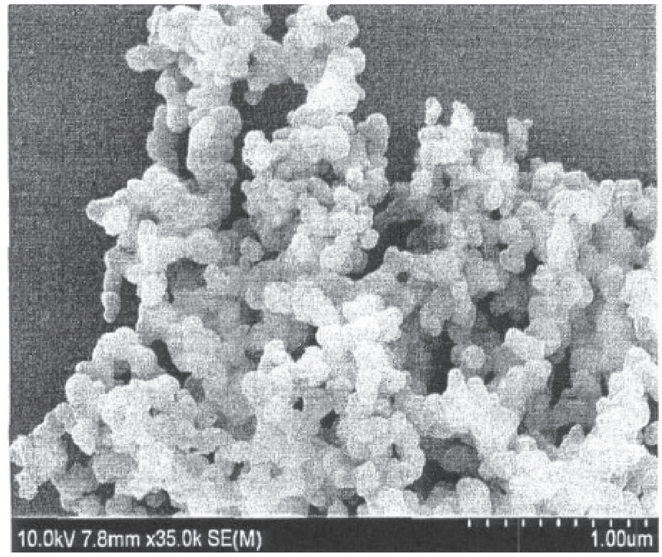

Fig. 6 – Scanning electron microscopy image of the silica product
Slika 6 – Slika proizvoda silicijeva dioksida snimljena skenirajućom elektronskom mikroskopijom

The SEM image showed that the product was in aggregation and the outline was not clear, which might be due to the internal temperature gradient of silica in the process of heating. Dehydration between the hydroxyl functional groups (OH–Si–OH) caused the aggregation of the particles, whose size was between 20 – 30 nm.

4. Conclusions

The alkali dissociation method is more suitable for the preparation of silica from oil shale residues than the acid dissociation method, because it results in a higher yield of SiO_2.

The optimum conditions for the preparation of silica from FS oil shale residue are as follows: temperature 100 °C,mass fraction of NaOH 8 %, and alkali dissolving time 5 h.

Through XRD, IR and SEM analysis, it was found that the produced silica had a purity of 98.4 % and a particle size between 20 – 30 nm, indicating the product is high-quality white carbon black.

List of symbols and abbreviations
Popis simbola i kratica

θ – scattering angle
– kut raspršenja

IR – infrared radiation
– infracrveno zračenje

XRD – x-ray diffraction
– rendgenska difrakcija

XRF – x-ray fluorescence
– rendgenska fluorescencija

SEM – scanning electron microscope
– skenirajući elektronski mikroskop

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SAŽETAK

Studija o pripravi silicijeva dioksida uporabom ostataka iz naftnih škriljevaca

Lei Nie i *Tong Wang* *

Uporabom naftnih (uljnih) škriljevaca nastaje obilje ostataka naftnog škriljevca, koji ne samo da mogu izravno uzrokovati ozbiljno onečišćenje okoliša, već i dovesti do gubitka resursa. U ovom radu provedena je usporedba metode izluživanja kiselinom i metode otapanja lužinom kako bi se dobili optimalni uvjeti za obradu i dobivanje bijele čađe, koji su određeni na sljedeći način: maseni udjel NaOH je 8 %, vrijeme otapanja u lužini je 5 h i temperatura reakcije 100 °C. Potom su analizirane karakteristike dobivene bijele čađe pomoću XRD-a, SEM-a i IR spektroskopije. Rezultati su pokazali da proizveden silicijev dioksid ima veličinu čestica 20 – 30 nm i čistoću od 98,4 %. Priprava visokokvalitetne bijele čađe dobar je način za postizanje dovoljnog i razumnog korištenja ostataka naftnog škriljevca, koje može imati brojne ekološke i društvene koristi.

Ključne riječi
Ostatci naftnog škriljevca, silicijev dioksid, otapanje lužinom, karakterizacija

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